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FINAL REPORT

to the

National Aeronautics and Space Administration

for

Grant NGR-22-009-091

"Surface Properties of Thermionic Electrodes"

for

November 1, 1964 to April 30, 1972

**CASE FILE
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Submitted by

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1. INTRODUCTION

During the past 7 1/2 years (November 1, 1964 to April 30, 1972), we have received a grant from NASA to perform research on the surface properties of thermionic electrodes. The objective of our work was to obtain analytical and experimental results that may contribute towards improving the performance of thermionic energy conversion devices. The results are summarized in this final report.

Although the value of a research program cannot be measured solely in terms of the number of publications or theses, these figures are worth mentioning. (Lists of publications and theses are given in the Appendix.)

Publications and Conference Presentations:

Journal Articles..... 15

Conference Presentations..... 10

Total..... 25

Theses

Bachelors..... 3

Masters..... 3

Doctors..... 4

Total 10

It is my personal belief that, aside from the educational benefits of our work, the most significant achievements were: (1) the development of a quasiequilibrium model which provides semiquantitative predictions of the reaction of oxygen with refractory metals at high temperature and low pressure¹⁻⁵; (2) the extensive experimental data⁶⁻¹⁷ obtained on the adsorption and work function properties for a wide variety of adsorbates

(Cs, K, Na, I, Br, Cl, O) on several refractory metals (W, Ta, Mo, and Re). We are quite certain that the value of the quasiequilibrium model and our experimental data on oxygen-metal reactions will not be limited to thermionic energy conversion, but will extend to a wide range of other technological devices and processes, such as high temperature nuclear reactors, incandescent and arc lamps¹⁸, chemical vapor deposition, and vacuum pressure measurements⁵. The potential technological value of our data on alkali metal adsorption appears to be far more limited; however, these data are of some value to science, particularly to the recent surge of interest in developing a detailed quantum mechanical description of adsorption.

We have very much enjoyed our relation with the people at the NASA Lewis Center, and we are especially grateful to Roland Breitwieser for his guidance and his belief in research at academic institutions.

2. EXPERIMENTAL STUDIES

2.1 Introductory Remarks

Throughout this research program we have concentrated primarily on obtaining detailed experimental data on the influence of cesium on the work functions of various refractory metals that were being considered for possible use as electrodes (i.e., thermionic emitters and/or collectors) in thermionic energy converters. Data of this nature are needed both by researchers attempting to develop a theoretical description of thermionic converters and by engineers attempting to build converters having improved performance. Since the development of a theoretical model of cesium adsorption would benefit from the availability of comparative data for other alkali metals, we also performed some experiments with Na and K. Single crystals were used in many of our studies because an objective was to determine the influence of surface crystallographic structure on the cesium adsorption properties [i.e., on the dipole moment (work function change) and on the binding energy (heat of adsorption) of the cesium-metal system]. These experimental studies of alkali metal adsorption are summarized in Section 2.2.

As this research program proceeded, we began to concentrate more on the adsorption of oxygen and of halogen gases on refractory metals. These studies were motivated by evidence that the presence of small amounts of oxygen (and possibly halogens) in thermionic converters result in substantial increases in power output. Additional data on the adsorption properties of these electronegative gases were needed to develop

a clearer understanding of the phenomena so that the highest possible increases could be achieved. We measured the work function change and desorption energy of oxygen and of halogens on various refractory metals, and, very recently, we have used Auger electron spectroscopy to obtain approximate measurements of the coverage of oxygen on tungsten as a function of oxygen pressure and tungsten temperature. These results for oxygen and halogen adsorption are summarized in Section 2.3. The model we have developed for the reaction of oxygen with refractory metals at high temperatures and low pressures is summarized in Section 3.

2.2 Experimental Studies of the Adsorption of Alkali Metals on Refractory Metals

We have used three different experimental techniques in our studies of the adsorption properties of alkali metals on refractory metals:

1. Cylindrical Thermionic Emission Microscope. This technique, illustrated in Fig. 1, was employed to measure the thermionic current emitted in different crystallographic directions from a single-crystal tungsten filament which was covered to varying degrees with adsorbed cesium⁹. The advantage of this technique was that it enabled us to observe the influence of crystallographic structure, cesium pressure, and filament temperature on the thermionic emission from tungsten (Figs. 2-4). The disadvantage was that quantitative interpretation of the data was complicated by the fact that the cesium coverage was not measured in this apparatus and we suspect that the coverage on a particular crystallographic region of the filament surface was influenced to some degree by surface diffusion to (or from) adjacent regions having different crystallographic orientation.
2. Contact Potential Technique. We utilized the electron beam retarding potential technique to measure the dependence of the work function of a metal surface on the coverage (concentration) of adsorbed alkali metal atoms^{8, 12-15}. This technique was an excellent complement to the thermionic emission microscope because it enabled us to determine the coverage and to work with single crystals that were sufficiently large, and at sufficiently

low temperature, to minimize the possible influence of surface migration between regions of different crystallographic structure.

On the other hand, the contact potential technique forced us to work at temperatures below the range of thermionic converters, and it did not allow us to determine the dependence of coverage on alkali metal pressure and electrode temperature. The apparatus is shown in Fig. 5, and the principal experimental results are presented in Figs. 6-10.

3. Molecular Beam Technique. This technique was used to determine the binding energy of cesium on tungsten single crystals^{12, 16}. The apparatus is shown in Fig. 11, and the characteristic desorption times measured for cesium on (110) and (100) tungsten crystals are given in Fig. 12. On the basis of these data, the desorption energy of cesium ions from tungsten is 2.05 eV for the (100) face and 1.77 eV for the (110) face. These results constitute a useful complement to the contact potential data, since the combined results provide a more complete description of the nature of the cesium-tungsten bond and its dependence on crystal structure¹⁶.

In Section 4.1 we comment on our attempts to interpret our experimental results in terms of various theoretical models.

2.3 Experimental Studies of the Interaction of Oxygen and Halogens with Refractory Metals

We have used four different experimental techniques in our studies of the interaction of oxygen and halogens with refractory metals:

1. Cylindrical Thermionic Emission Microscope. This technique, which was described in the preceding section, was utilized to measure the thermionic current emitted in different crystallographic directions from a single-crystal tungsten filament which was covered to varying degree with adsorbed oxygen¹⁰. The objective was to determine the dependence of the thermionic emission from tungsten on crystallographic structure, oxygen pressure, and filament temperature (Figs. 13 and 14). By assuming that the work function change was directly proportional to the oxygen coverage, we were able to estimate the effective desorption energy for oxygen on tungsten (Fig. 15) from measurements of the rate of change of the emission current when the oxygen pressure is suddenly decreased. As in the case of cesium, quantitative interpretation of these data was prevented by the fact that the oxygen coverage could not be measured in this apparatus and we suspect that the coverage on a particular crystallographic region of the filament surface was influenced substantially by surface diffusion of oxygen to (or from) adjacent regions having different crystallographic orientations¹⁰.
2. Cylindrical Thermionic Diodes. The preceding technique was simplified by replacing the single-crystal tungsten filament with polycrystalline filaments of molybdenum, tantalum, rhenium,

and tungsten, thereby enabling us to obtain data of the influence of oxygen on the work function of a variety of refractory

metals¹¹ (Fig. 16). We also obtained estimates of the effective desorption energy for oxygen on these metals¹¹; 5.75 ± 0.25 eV for O-Mo; 5.5 ± 0.15 eV for O-Re; 6.05 ± 0.1 eV for O-W.

3. Contact Potential Technique. The apparatus described in Section 2.2 and illustrated in Fig. 5 was also used to measure the work function change resulting from the adsorption of oxygen on a tantalum (110) crystal⁷ and of iodine, bromine, and chlorine on a tungsten (100) crystal.¹³ (Figs. 17-20). By heating the crystal we were able to observe the stages of desorption of the halogens from tungsten¹³.
4. Auger electron spectroscopy. We have recently used this technique to determine the oxygen coverage on tungsten as a function of the oxygen pressure and the tungsten temperature¹⁷. As shown in Fig. 21 the Auger peak corresponding to oxygen decreases with increasing temperature of the tungsten sample. Data for a range of pressures and temperatures are included in Fig. 22, and, if we assume that the peak-to-peak height of the oxygen Auger peak is directly proportional to the oxygen coverage on the tungsten surface, then these data correspond to adsorption isobars. These results lead to a simple model which provides a consistent description of the data in the low coverage range¹⁷. We believe that this work is the first demonstration that chemical analysis of solid surfaces by Auger electron spectroscopy may be performed for samples at

extremely high temperatures (2500°K in the present case).

A summary of our analytical studies of the reaction of oxygen with
refractory metals is presented in Section 3.

2.4 Experimental Studies of the Adsorption of Cesium-Oxygen Mixtures on Refractory Metals

These studies were motivated by evidence that the power output of a thermionic energy converter increases significantly when a small amount of oxygen is added. We performed a number of experimental measurements of the influence of mixtures of cesium and either oxygen⁸ or halogens¹³ on the work function of tantalum and tungsten, but the results generally were not reproducible as a result of side effects (e.g., contamination of the surface by unidentified* impurities displaced from the chamber walls by cesium or oxygen). Our most reliable data are displayed in Figs. 23-25, and we observe that oxygen and halogens do have a very marked effect on the work function of cesium-metal systems.

* At the time of these experiments, we did not have an Auger electron spectrometer to identify the impurities.

3. ANALYTICAL STUDIES

When gaseous oxygen reacts with refractory metals at high temperature, the metal oxide molecules formed at the surface evaporate so readily that a surface oxide film does not form. These reactions have been studied quite extensively because they are encountered in a variety of technological problems, including thermionic energy conversion, high-temperature power and propulsion systems, and high-speed flight. To obtain a consistent description of the existing experimental data, we have developed a quasiequilibrium model¹⁻³ of the reaction of gases with metals at high temperature where the oxide products are volatile. The principal attribute of this model is that it provides semiquantitative predictions of the rate of attack (erosion) of a refractory metal as a function of pressure and temperature.

The quasiequilibrium model is based on the assumption that a fraction (ζ) of the O_2 molecules striking a metal surface will be adsorbed and undergo chemical reaction, whereas the remainder ($1 - \zeta$) will rebound from the surface without undergoing chemical reaction. Furthermore, it is assumed that the fraction that adsorbs and reacts can be considered to attain local thermodynamic equilibrium with the metal, with the consequence being that the rates of evaporation of the various reaction products (O , O_2 , WO , WO_2 , WO_3 , etc.) correspond to the rates at which these species would effuse from the orifice of a Knudsen (equilibrium) cell at the same temperature as the metal. As shown in detail in references 1 and 3, these assumptions enable us to compute these rates if the free energies of formation are available for each product, and if we determine the adsorption

fraction, ζ , by a semiempirical scheme which is consistent with the model^{*}. The results agree satisfactorily with existing mass spectrometric measurements of the rates of evaporation of products from tungsten (Fig. 26) and from molybdenum¹. In addition, the results provide a reasonably accurate description of experimental data on the rate of volatilization (e.g., erosion) of tungsten by oxidation for a wide range of temperature and pressure³ (Fig. 27). The model has also been applied to the reaction of fluorine with tungsten¹⁹ (Fig. 28) and the reaction of oxygen with rhenium⁴.

* To obtain a more quantitative description of ζ for O_2 on tungsten, we utilized Auger electron spectroscopy to obtain data on the oxygen coverage as a function of pressure and temperature (Section 2.3 and ref. 17).

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Alkali Metal Adsorption

Although the adsorption of alkali metals on metal surfaces has been studied by many investigators using a variety of techniques, the results do not yet provide a description which is consistent, detailed, and reliable. We believe that very small degrees of surface contamination may be responsible for some discrepancies between the data obtained by different investigators¹⁴. Furthermore, we believe that adsorption data obtained by field emission techniques do not provide an accurate representation of adsorption on large, planar crystals¹⁵. Our biased conclusion is that the contact-potential data obtained in the present program are the most reliable data now available on the adsorption of alkali metals on tantalum (110) and tungsten (100) crystals. However, additional data for other crystal faces are necessary to provide a more complete picture of alkali metal adsorption and thereby guide the development of adsorption theory. Future studies should incorporate a wide variety of modern surface science techniques, such as Auger electron spectroscopy, electron diffraction, flash desorption mass spectrometry, and modulated molecular beam techniques.

We were disappointed in our attempts to compare our experimental data with the predictions of existing theoretical models of alkali metal adsorption. (For detailed discussions of our comparisons, see references 15, 16, and 20). We found that some theoretical models could not be applied

because they required extensive computation, while other models did not yield predictions that agreed satisfactorily with our data (except possibly in the limit of low coverage). Many of the theoretical models involve adjustable parameters which prevent us from performing a rigorous test of the model until reliable experimental data are available for a wider range of materials. Although it is clear that more theoretical work is needed, we believe that it is equally important to obtain additional experimental data on the adsorption properties (work function change, binding energy, etc.) of various alkali metals on different crystal faces of tungsten, molybdenum, rhenium, etc. The particular systems should be carefully chosen to provide the experimental data that will be most useful in testing the present theoretical models and guiding future developments. In reference 16 we point out that a more stringent test of theoretical models is obtained by measuring different properties of the adsorption bond, such as the dipole moment (work function change) and the binding energy (desorption energy).

4.2 Oxygen Adsorption

We believe that the quasi-equilibrium model represents a significant step forward in clarifying our understanding of the interaction of oxygen (and halogens) with refractory metals. This model could be improved by performing investigations that would lead to a more quantitative understanding of ζ , the adsorption (or equilibration) probability. Experiments utilizing molecular beam techniques and Auger electron spectroscopy would provide the data needed to guide the formulation of a model of the adsorption

step.

The quasi-equilibrium model does not provide information on the dependence of the work function of a surface on oxygen coverage. This important problem is, most likely, an extremely difficult theoretical task, and it may be best to concentrate first on obtaining experimental data. As indicated by the results of our recent study described in Section 2.3, Auger electron spectroscopy is an extremely useful technique for determining the coverage of oxygen on a particular metal as a function of oxygen pressure and metal temperature. By measuring the thermionic emission current from the same surface as a function of pressure and temperature, we would be able to determine the dependence of work function on coverage.

4.3 Adsorption of Cesium-Oxygen Mixtures

The prediction or interpretation of the performance (e.g., current-voltage characteristics) of a thermionic energy converter containing cesium + oxygen requires knowledge of the dependence of the emitter work function on the cesium and oxygen pressures and on the emitter temperature. This knowledge is incomplete at present because of the scarcity of experimental data, and our limited data for Cs + O on Ta(110) do no more than illustrate the complexity of the problem. Although our data for the separate adsorption of cesium and of oxygen are necessary auxiliary information, they do not satisfy the need for data on co-adsorption of the species. We suspect that this complex adsorption case will be understood only if considerable effort is devoted to it using a variety of experimental

techniques. Since the cost of such an effort may be too high to be justified, we suspect that it may be necessary to settle for less

detailed information based on careful experiments performed in thermionic diodes.

5. REFERENCES

1. "Quasiequilibrium Treatment of Gas-Solid Reactions : I. Evaporation Rates of Volatile Species Formed in the Reaction of O_2 with W, Mo, and C", J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4475 (1969).
2. "Quasiequilibrium Treatment of Gas-Solid Reactions: II. Flash Desorption of Oxidation Products for a Tungsten Surface", J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4485 (1969).
3. "Quasiequilibrium Treatment of Gas-Solid Reactions: III. Rate of Volatilization of Tungsten by High-Temperature Oxidation", J. C. Batty and R. E. Stickney, Oxidation of Metals 3, 331 (1971).
4. "A Simplified Experimental Method for Determining the Thermochemical Properties of Certain Volatile Species; Application to ReO_2 and ReO_3 ", J. E. Franklin and R. E. Stickney, High Temperature Science 3, 401 (1971).
5. "Analysis of the 'Oxygen Pumping Effect' of Tungsten Cathodes in Ionization Gauges and Mass Spectrometers", A. E. Dabiri and R. E. Stickney, J. Vac. Sci. Technol. (in press).
6. "Effect of Fluorine and Oxygen on the Work Function of Polycrystalline Tungsten", J. G. Bergman and R. E. Stickney, in Report on the 26th Annual Conference on Physical Electronics (M.I.T. 1966), pp. 299-305.
7. "Contact-Potential Measurements of the Adsorption of Cs, O_2 , and H_2 on (110)Ta", D. L. Fehrs and R. E. Stickney, Surface Sci. 8, 267-287 (1967).
8. "Experimental Measurements of the Work Functions and Desorption Energies of the Systems O-W, O-Ta, and Cs-O-Ta", R. E. Stickney, W. Greaves, and D. L. Fehrs, in Report on 1967 Thermionic Conversion Specialist Conference (IEEE, 1967) pp. 138-144.
9. "Adsorption Studies Based on Thermionic Emission Measurements: I. Cesium on Single-Crystal Tungsten", J. L. Coggins and R. E. Stickney, Surface Sci. 11, 355-369 (1968).
10. "Adsorption Studies Based on Thermionic Emission Measurements: II. Oxygen on Single-Crystal Tungsten", W. Engelmaier and R. E. Stickney, Surface Sci. 11, 355-369 (1968).
11. "Adsorption Studies Based on Thermionic Emission Measurements: III. Oxygen on Polycrystalline W, Mo, Ta, and Re", W. Greaves and R. E. Stickney, Surface Sci. 11, 395-410 (1968).
12. "Measurements of the Work Function and Desorption Energy of Cesium and Potassium on (100) Tungsten", D. L. Fehrs, T. J. Lee, and R. E. Stickney, in Report on 1968 Thermionic Conversion Specialist Conference (IEEE, 1968), pp. 10-17.

13. "Contact-Potential Measurements of the Adsorption of I_2 , Br_2 , and Cl_2 on Bare and Cesiumated W(100)", D. L. Fehrs and R. E. Stickney, Surface Sci. 17, 298 (1969).
14. "Comments on 'An Electron Diffraction Study of Cesium Adsorption on Tungsten'", D. L. Fehrs, T. J. Lee, B. J. Hopkins, and R. E. Stickney, Surface Sci. 21, 197 (1970).
15. "Contact-Potential Measurements of the Adsorption of Alkali Metals on Ta(110) and W(100) Crystals", D. L. Fehrs and R. E. Stickney, Surface Sci. 24, 309 (1971).
16. "Molecular Beam Study of the Desorption of Cesium Ions from Tungsten Crystals", T. J. Lee and R. E. Stickney, Surface Sci. (in press).
17. "Measurements of the Coverage of Oxygen on Tungsten at High Temperature and Low Pressure", A. E. Dabiri, V. S. Aramati, and R. E. Stickney, paper presented at 1972 Physical Electronics Conference, Albuquerque, New Mexico, March 1972. (To be submitted for publication in Surface Science).
18. We now have a grant from Sylvania for investigations of chemical reactions of halogen-oxygen mixtures with tungsten and other materials used in incandescent and arc lamps.
19. "Quasiequilibrium Analysis of the Reaction of Atomic and Molecular Fluorine with Tungsten", P. C. Abbott and R. E. Stickney, J. Phys. Chem. (submitted).
20. "Contact-Potential Measurements of the Adsorption of Cs, K, and Na on Ta(110)", doctoral thesis, Mechanical Engineering Department, M.I.T., January 1968.

Appendix: List of Journal Articles, Conference Presentations, and
Theses on Work Partially Supported by Present Grant

1. "Contact-Potential Measurements of the Adsorption of Cs, O₂, and H₂ on (110)Ta", D. L. Fehrs and R. E. Stickney, Surface Sci. 8, 267-287 (1967).
2. "Adsorption Studies Based on Thermionic Emission Measurements: I. Cesium on Single-Crystal Tungsten", J. L. Coggins and R. E. Stickney, Surface Sci. 11, 355-369 (1968).
3. "Adsorption Studies Based on Thermionic Emission Measurements: II. Oxygen on Single-Crystal Tungsten", W. Engelmaier and R. E. Stickney, Surface Sci. 11, 370-394 (1968).
4. "Adsorption Studies Based on Thermionic Emission Measurements: III. Oxygen on Polycrystalline W, Mo, Ta, and Re", W. Greaves and R. E. Stickney, Surface Sci. 11, 395-410 (1968).
5. "Quasiequilibrium Treatment of Gas-Solid Reactions: I. Evaporation Rates of Volatile Species Formed in the Reaction of O₂ with W, Mo, and C", J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4475 (1969).
6. "Quasiequilibrium Treatment of Gas-Solid Reactions: II. Flash Desorption of Oxidation Products for a Tungsten Surface", J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4485 (1969).
7. "Contact-Potential Measurements of the Adsorption of I₂, Br₂, and Cl₂ on Bare and Cesiumated W(100)", D. L. Fehrs and R. E. Stickney, Surface Sci. 17, 298 (1969).
8. "Comments on 'An Electron Diffraction Study of Cesium Adsorption on Tungsten'", D. L. Fehrs, T. J. Lee, B. J. Hopkins, and R. E. Stickney, Surface Sci. 21, 197 (1970).
9. "Contact Potential Measurements of the Adsorption of Alkali Metals on Ta(110) and W(100) Crystals", D. L. Fehrs and R. E. Stickney, Surface Sci. 24, 309 (1971).
10. "Quasiequilibrium Treatment of Gas-Solid Reactions: III. Rate of Volatilization of Tungsten by High-Temperature Oxidation", J. C. Batty and R. E. Stickney, Oxidation of Metals 3, 331 (1971).
11. "A Simplified Experimental Method for Determining the Thermochemical Properties of Certain Volatile Species; Application to ReO₂ and ReO₃", J. E. Franklin and R. E. Stickney, High Temperature Science 3, 401 (1971).

12. "Quasiequilibrium Analysis of the Reaction of Atomic and Molecular Fluorine with Tungsten", P. C. Abbott and R. E. Stickney, J. Phys. Chem. (submitted).
13. "Analysis of the 'Oxygen Pumping Effect' of Tungsten Cathodes in Ionization Gauges and Mass Spectrometers", A. E. Dabiri and R. E. Stickney, J. Vac. Sci. Technol. (in press).
14. "Molecular Beam Study of the Desorption of Cesium Ions from Tungsten Crystals", T. J. Lee and R. E. Stickney, Surface Sci. (in press).
15. "Measurements of the Coverage of Oxygen on Tungsten at High Temperature and Low Pressure", A. E. Dabiri, V. S. Aramati, and R. E. Stickney, (to be submitted to Surface Sci.)

Conference Presentations

Physical Electronics Conference:

<u>Year</u>	<u>Title</u>	<u>Authors</u>
1965	Thermionic Characteristics of the (110) and (112) Directions of Tungsten in Cesium Vapor	J. L. Coggins and R. E. Stickney
1966	Thermionic and Adsorption Characteristics of a Single-Crystal Tungsten Filament Exposed to Oxygen	W. Engelmaier and R. E. Stickney
1966	Contact-Potential Measurements of the Work Function of Tantalum as a Function of Cesium Coverage	D. L. Fehrs and R. E. Stickney
1966	Effect of Fluorine and Oxygen on the Work Function of Polycrystalline Tungsten	J. G. Bergman and R. E. Stickney
1967	Contact-Potential Measurements of the Adsorption of Cs and O ₂ on (110) Ta	D. L. Fehrs and R. E. Stickney
1968	Contact-Potential Measurements of the Adsorption of Cs, K, and Na on (110) Ta	D. L. Fehrs and R. E. Stickney
1969	Quasi-Equilibrium Model of the Reaction of Gaseous Oxygen with a Tungsten Surface	J. C. Batty and R. E. Stickney
1972	Measurements of the Coverage of Oxygen on Tungsten at High Temperature and Low Pressure	A. E. Dabiri and R. E. Stickney

Thermionic Conversion Specialist Conference:

1967	Experimental Measurements of the Work Functions and Desorption Energies of the Systems O-W, O-Mo, O-Re, O-Ta, and Cs-O-Ta	R. E. Stickney, W. Greaves, and D. L. Fehrs
1968	Measurements of the Work Function and Desorption Energy of Cesium and Potassium on (100) Tungsten	D. L. Fehrs, T. J. Lee, and R. E. Stickney

Doctoral Theses

1. J. L. Coggins, "Thermionic Emission from a Tungsten Monocrystal in Cesium Vapor", 1965.
2. J. W. Gadzuk, "Many-Body Theory of a Rapidly Varying, Inhomogeneous Electron Gas", 1967. (Prof. G. Koster, M.I.T. Physics Department, was co-supervisor).
3. D. L. Fehrs, "Contact-Potential Measurements of the Adsorption of Cs, K, and Na on (110) Ta", 1968.
4. J. C. Batty, "A Quasi-equilibrium Treatment of Gas-Solid Interactions", 1969.

Masters Theses

1. W. Englemaier, "Thermionic and Adsorption Characteristics of a Single-Crystal Tungsten Filament Exposed to Oxygen," 1966.
2. F. J. Walker, Jr., "Thermionic Studies of Oxygenated Tungsten and Rhenium in a Cesium Atmosphere", 1969.
3. V. S. Armati, "Development and Application of an Auger Electron Spectrometer for High Temperature Adsorption Studies", 1971.

Bachelors Theses

1. A. A. Aponick, "An Oxidation Study of a Tungsten Filament", 1963. (Electrical Engineering Department).
2. H. C. Jukvam-Wold, "Neutralization of Space Charge in Thermionic Energy Converters", 1966.
3. S. Rao, "High-Temperature Creep Properties of Tungsten in Vacuum and Oxygen Environments", 1970.

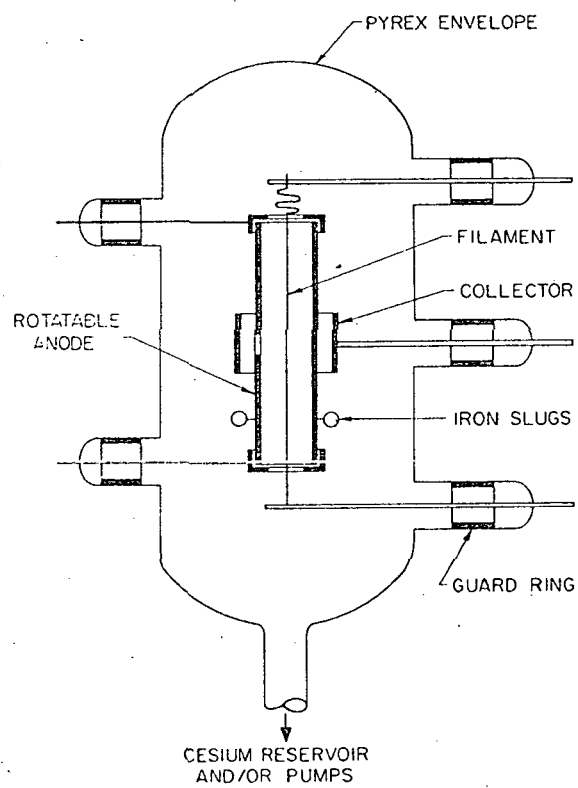


Fig. 1. Schematic diagram of cylindrical thermionic emission tube. [From Coggins and Stickney ⁹]

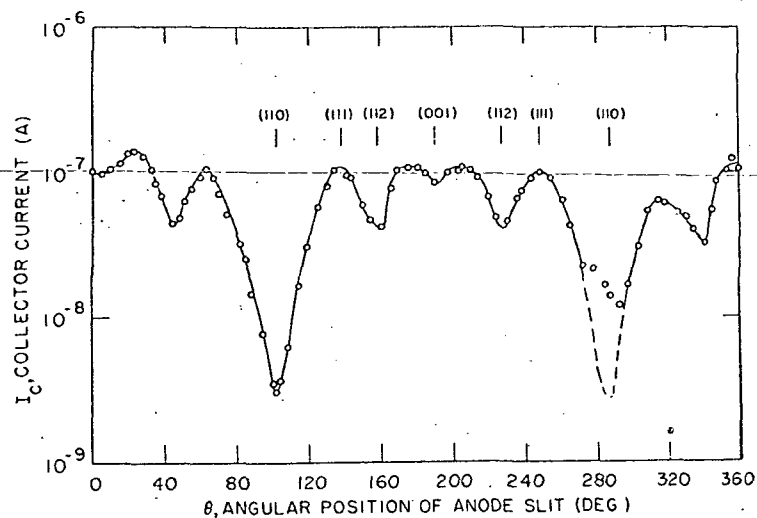


Fig. 2. Emission pattern for bare tungsten; $T = 1900^\circ\text{K}$. The indicated positions of different crystallographic directions were determined by comparison with the results of Nichols and Smith. [From Coggins and Stickney⁹]

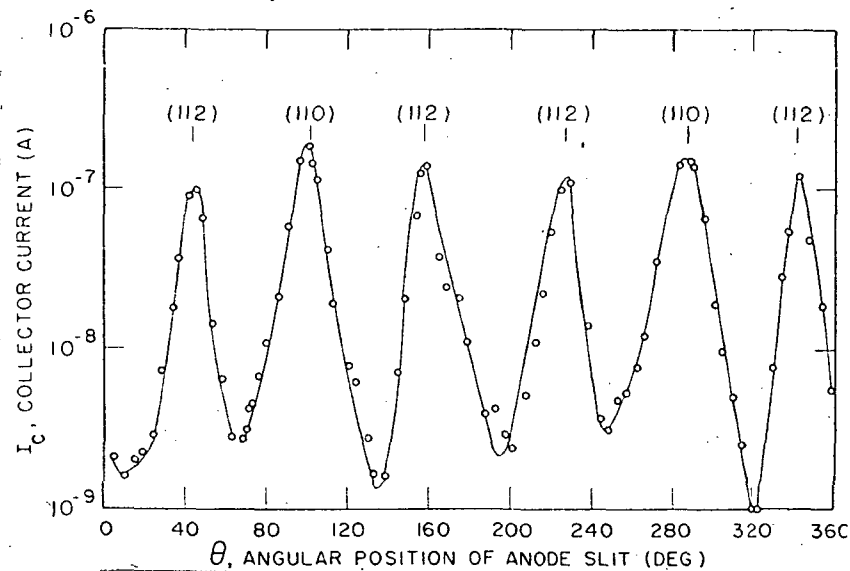


Fig. 3. Emission pattern for cesiated tungsten; $T = 750^\circ\text{K}$, $T_{\text{Cs}} = 296.7^\circ\text{K}$ ($p_{\text{Cs}} \approx 1.3 \times 10^{-6} \text{ Torr}$). Notice that the emission is highest in the (110) and (112) directions; as seen in Fig. 2, these directions have the lowest emission when the surface is bare (i.e., when no cesium is present). [From Coggins and Stickney⁹]

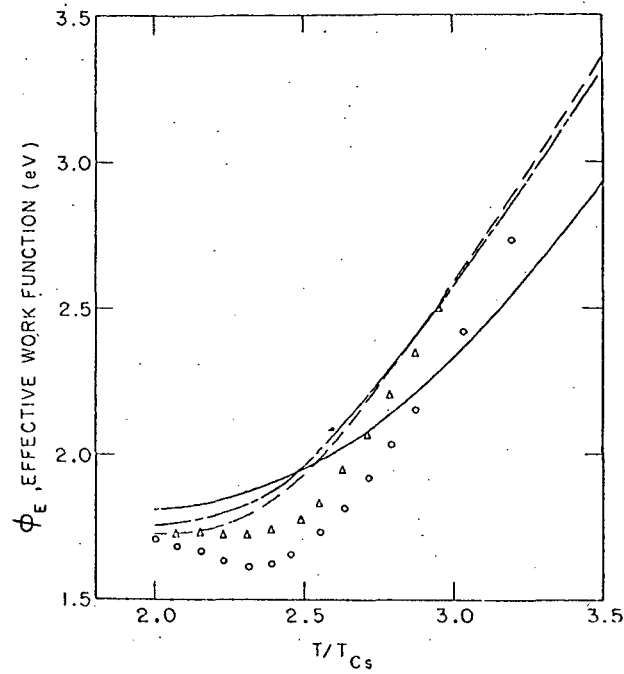


Fig. 4. Comparison of experimental results of the present study with theoretical predictions of ϕ_E vs. T/T_{Cs} . Circles and triangles represent data for (110) and (112) directions, respectively. (---) Rasor-Warner theory for $\phi_0 = 4.62$ eV; (—) Rasor-Warner theory for $\phi = 5.05$ eV; (— · —) Levine-Gyftopoulos theory for $\phi_0 = 5.30$ eV, $\sigma_f = 4.8 \times 10^{14} \text{ cm}^{-2}$, and $\phi_f = 1.8$ eV. [From Coggins and Stickney⁹]

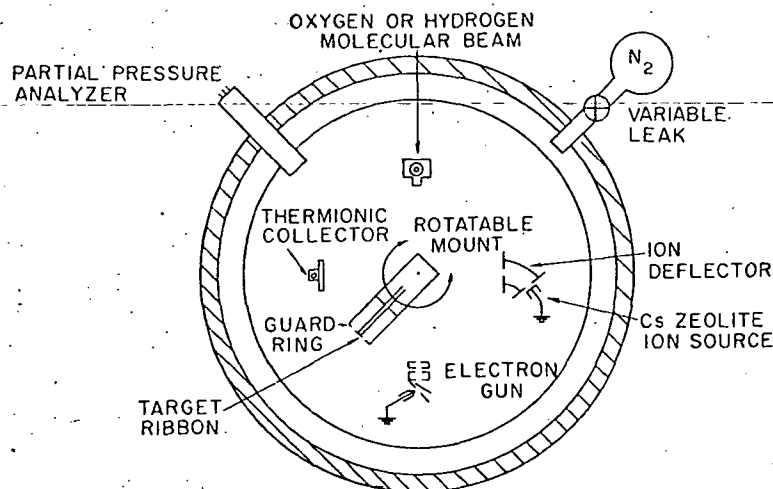


Fig. 5. Schematic of ultrahigh vacuum apparatus for contact potential measurements of the work function vs. coverage for various metals and adsorbates. [From Fehrs and Stickney⁷.]

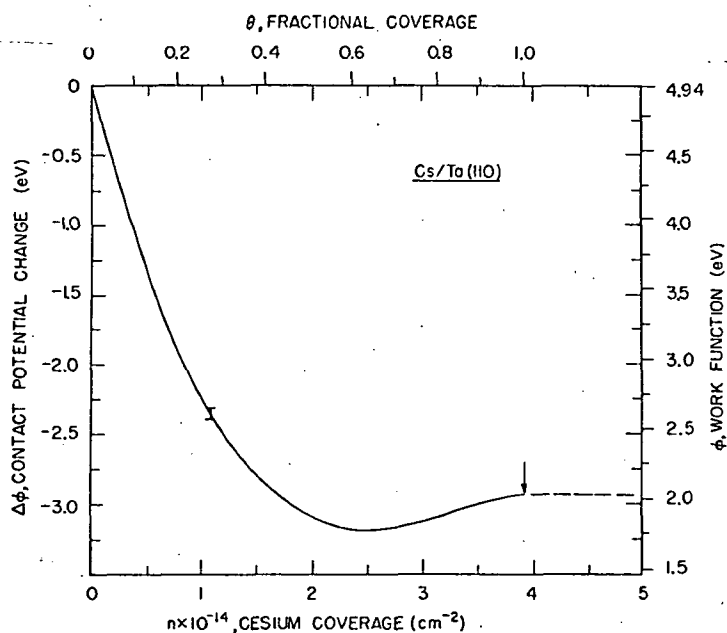


Fig. 6. Experimental data on $\Delta\phi$ versus n for the system Cs/Ta (110) at $\sim 300^\circ\text{K}$. The arrow denotes our estimate of the state $(\Delta\phi, n_f)$ corresponding to the high coverage limit. [From Fehrs and Stickney^{7,15}]

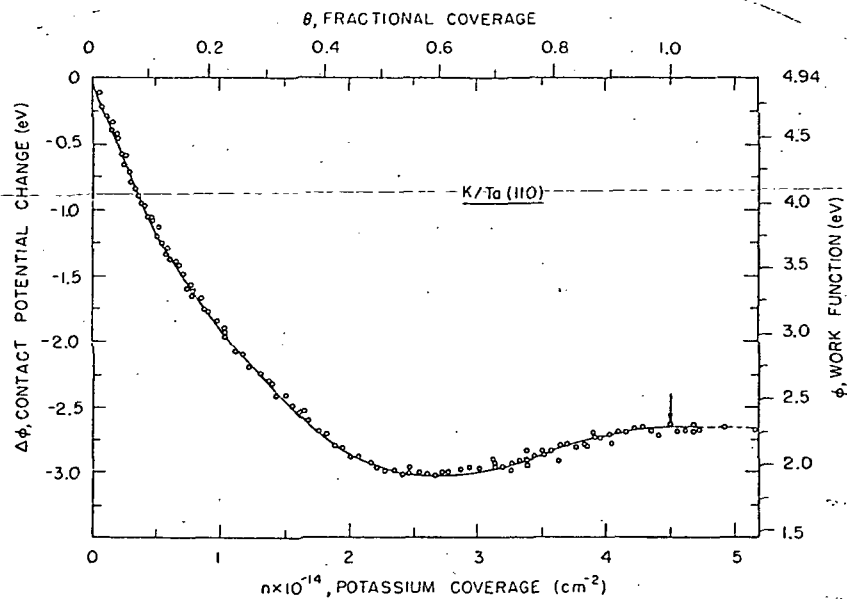


Fig. 7. Experimental data on $\Delta\phi$ versus n for the system K/Ta (110) at $\sim 300^\circ\text{K}$. The arrow indicates our estimate of the state ($\Delta\phi_f$, n_f) corresponding to the high coverage limit. [From Fehrs and Stickney¹⁵.]

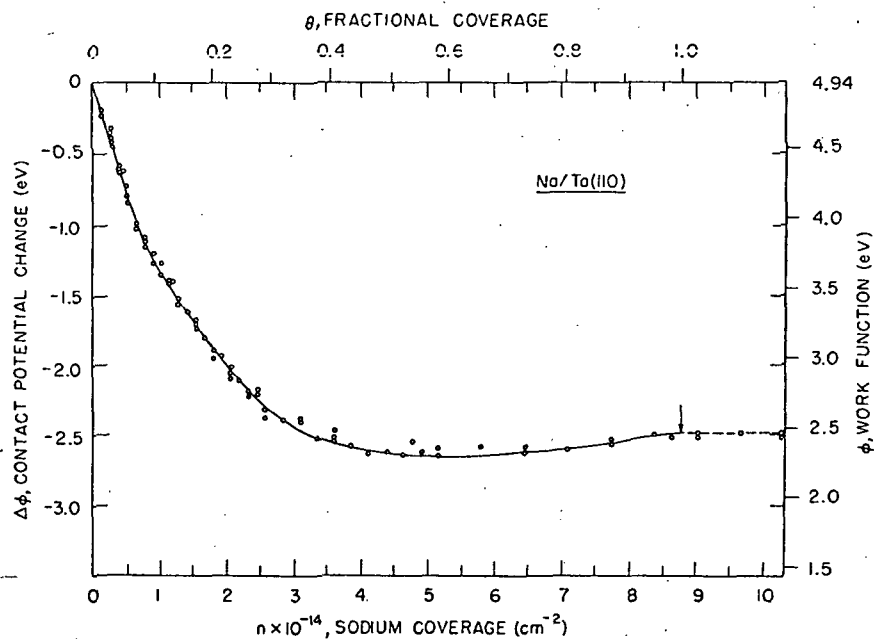


Fig. 8. Experimental data on $\Delta\phi$ versus n for the system Na/Ta(110) at 300°K . [From Fehrs and Stickney¹⁵.]

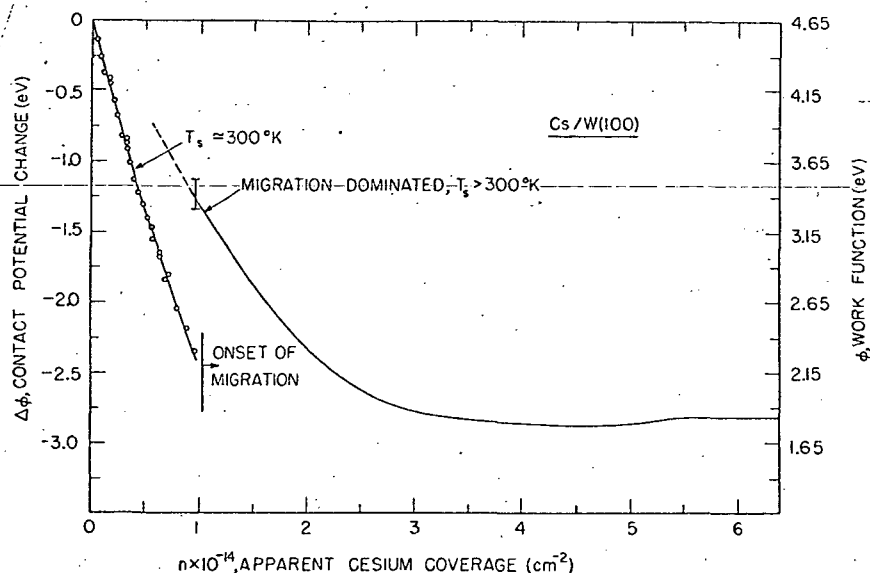


Fig. 9. Experimental data on $\Delta\phi$ versus n for the system Cs/W(100) at $\sim 300^\circ\text{K}$. Although the right-hand curve is distorted by surface migration, we believe that the left-hand curve accurately depicts $\Delta\phi$ versus n for $n \lesssim 0.8 \times 10^{-14} \text{ cm}^{-2}$. [From Fehrs and Stickney¹⁵].

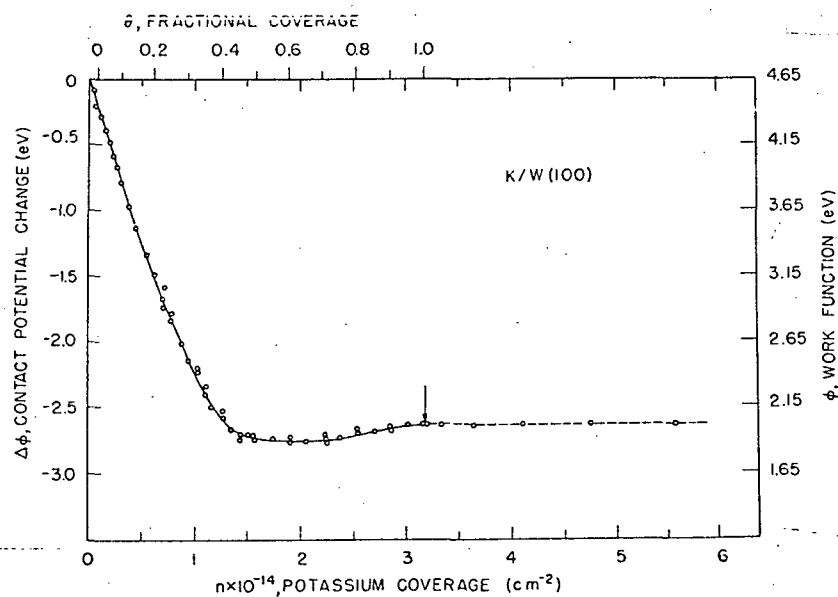


Fig. 10. Experimental data on $\Delta\phi$ versus n for the system K/W(100) at $\sim 300^\circ\text{K}$. [From Fehrs and Stickney¹⁵].

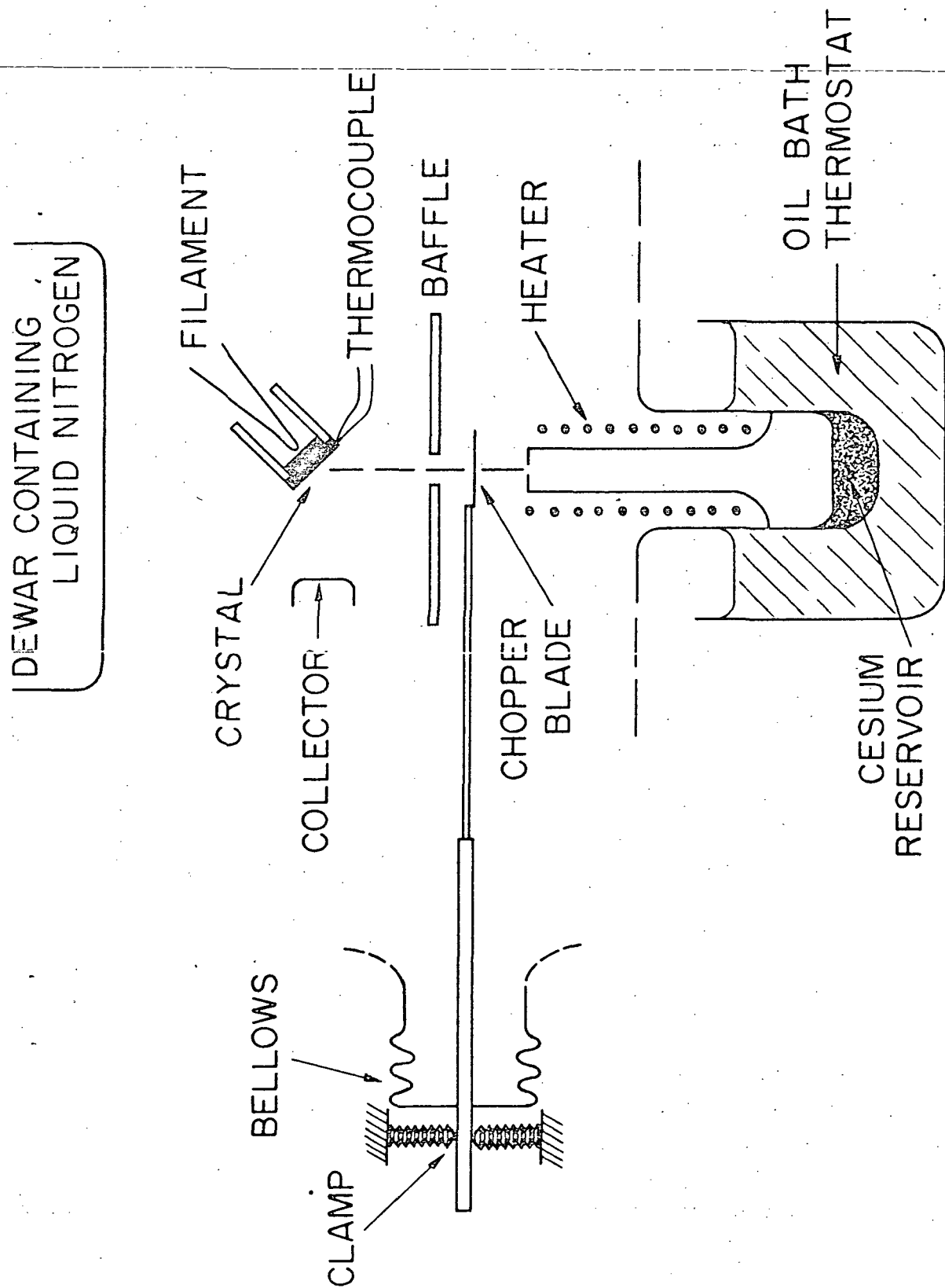


Fig. 11. Principal features of a modulated molecular beam apparatus for measuring the rate of desorption of Cs^+ from W crystals. (Not to scale.) The chopper is driven by an electromechanical vibrator located at the end of the chopper rod outside the vacuum chamber; the motion of the chopper is perpendicular to the plane of this figure. [From Lee and Stickney¹⁶.]

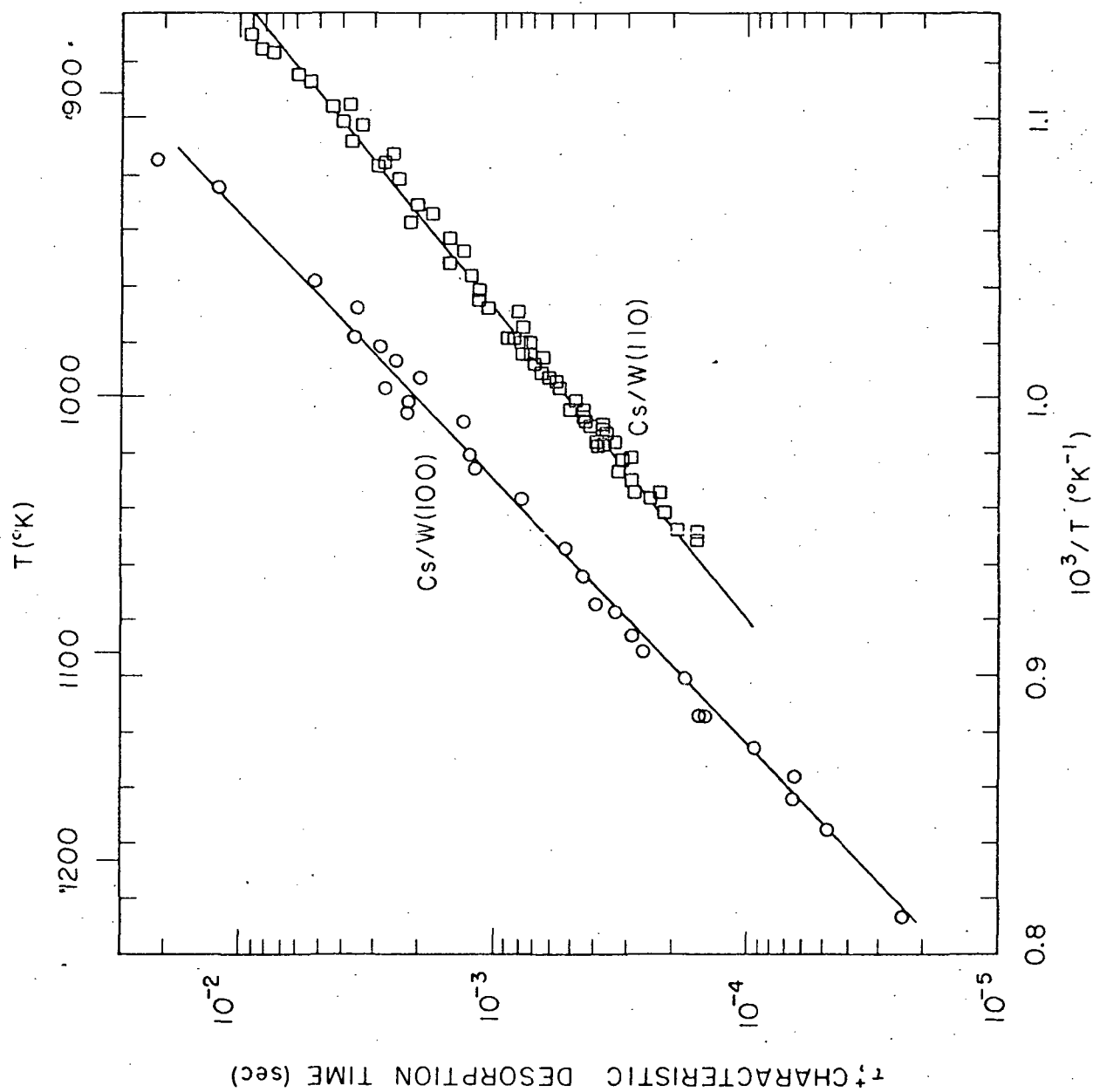


Fig. 12. Experimental data on $\log \tau$ vs $1/T$ for the desorption of Cs^+ from W(100) and W(110) crystals. [From Lee and Stickney¹⁶.]

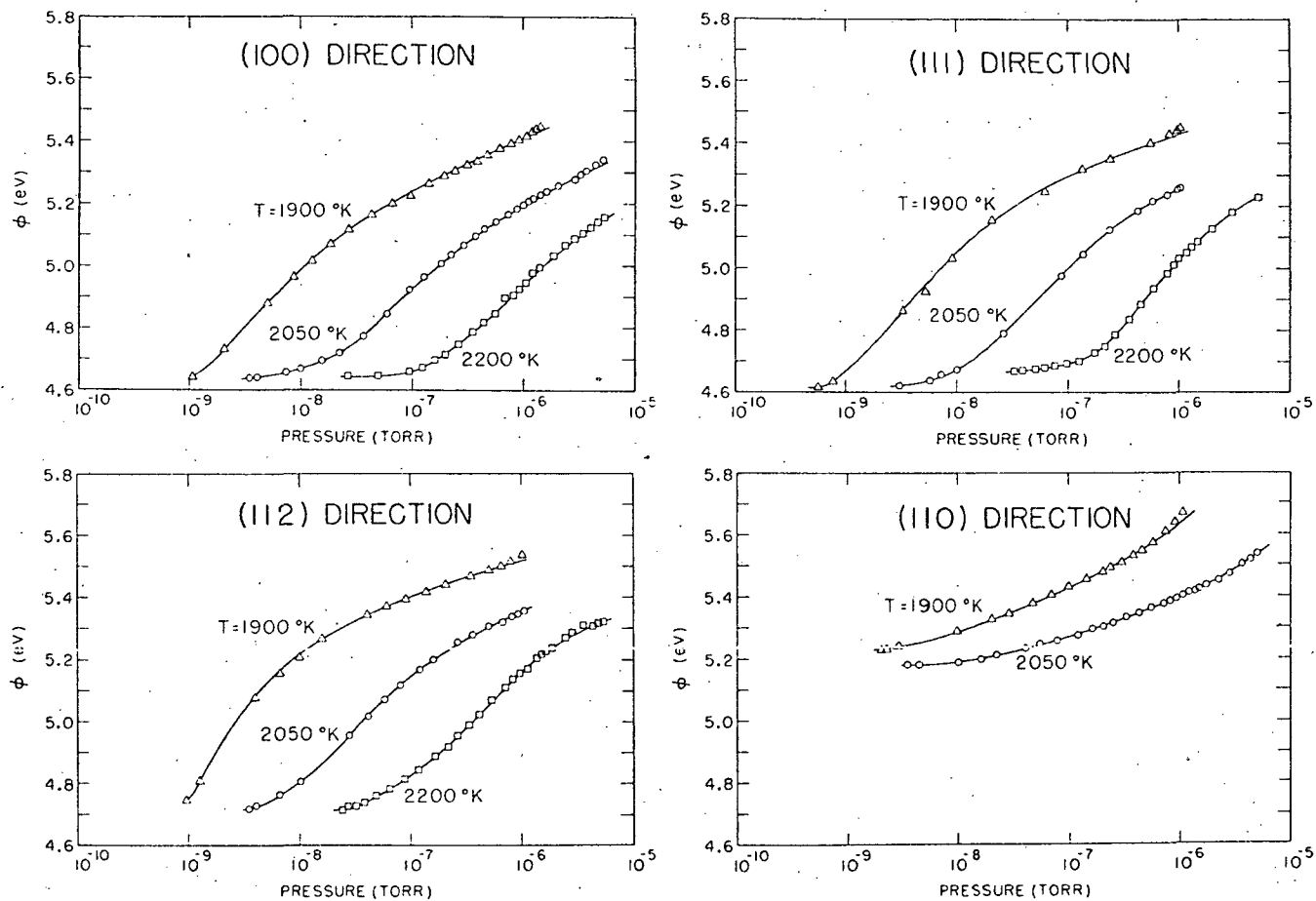


Fig. 13. Dependence of the effective work function, ϕ , on oxygen pressure and filament temperature, T , for the (100), (111), (112) and (110) crystallographic directions of tungsten. [From Engelmaier and Stickney¹⁰.]

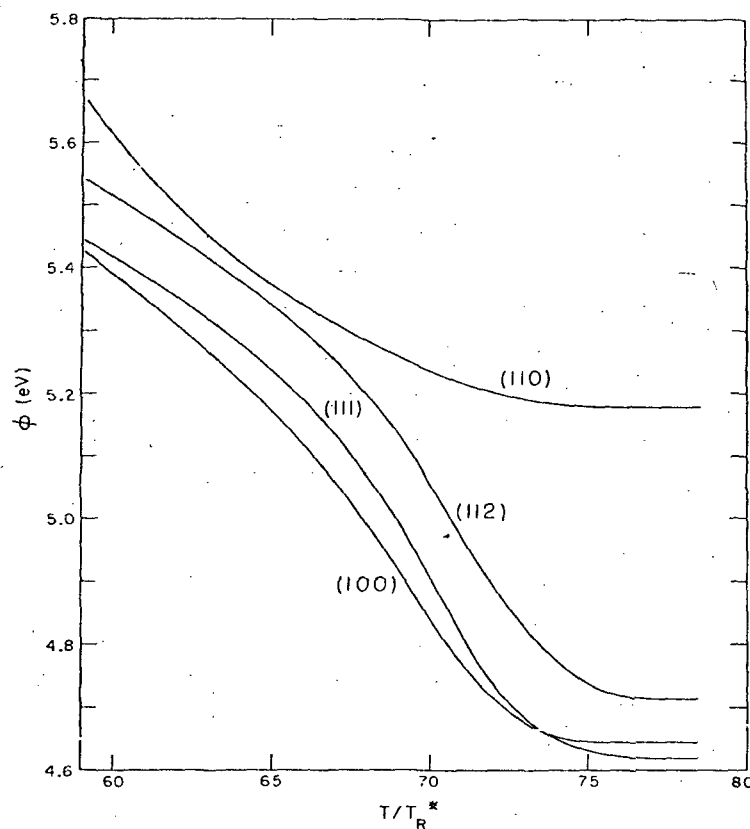


Fig. 14. Summary of the experimental results on the dependence of ϕ on T/T_R^* for various crystallographic directions of tungsten. T is the temperature of the tungsten filament, and T_R^* is the effective "reservoir temperature" for O_2 (i.e., the saturation temperature corresponding to the particular value of O_2 pressure). [From Engelmaier and Stickney¹⁰.]

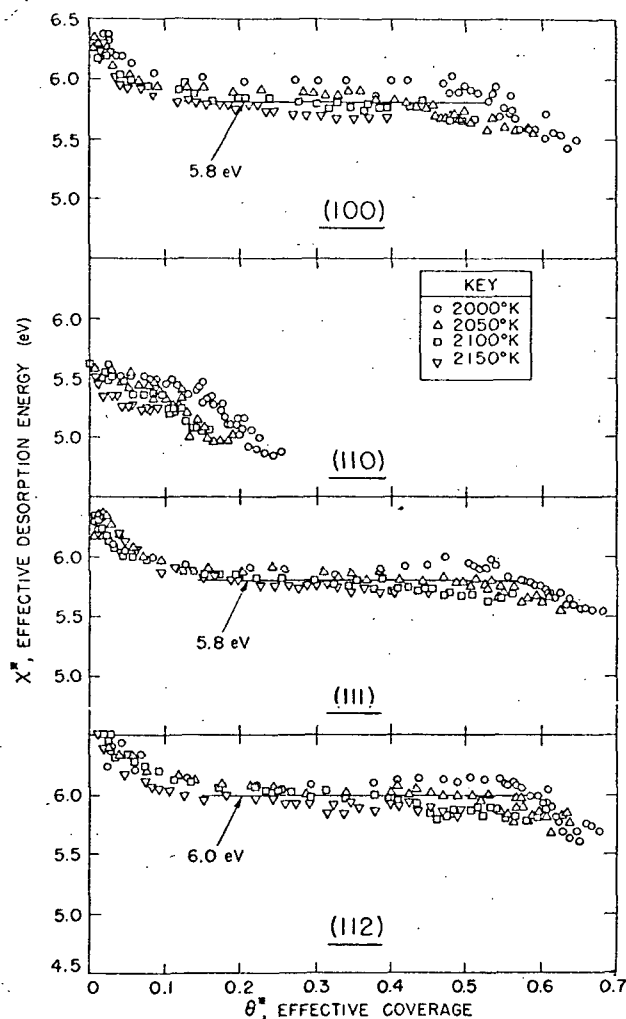


Fig. 15. Dependence of effective desorption energy on effective coverage for oxygen on the (100), (110), (111), and (112) crystallographic directions of tungsten. Horizontal lines are drawn through the data points to illustrate both the magnitude and constancy of χ^* . [From Engelmaier and Stickney¹⁰].

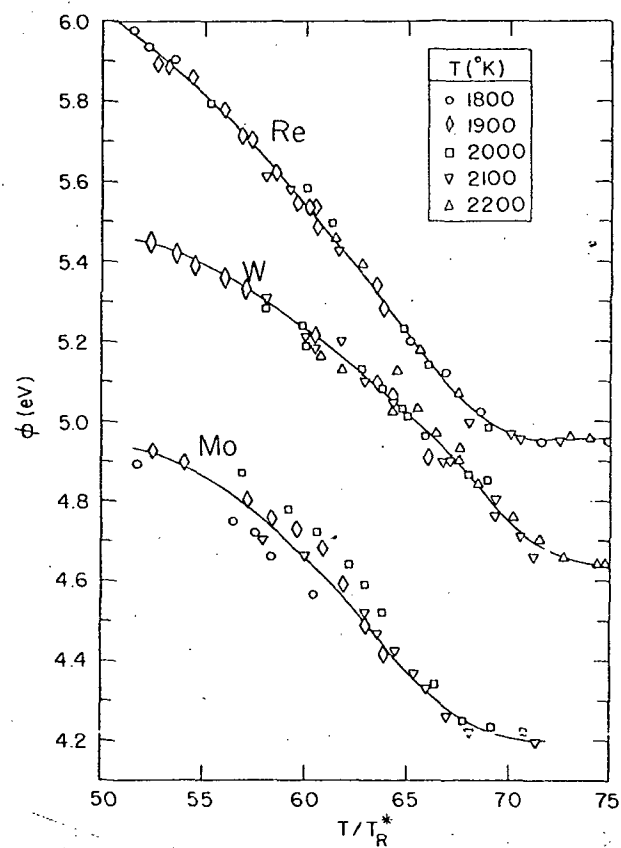


Fig. 16. Dependence of the effective work functions of polycrystalline W, Re, and Mo on T/T_R^* , where T and T_R^* are defined in Fig. 14. [From Greaves and Stickney¹¹.]

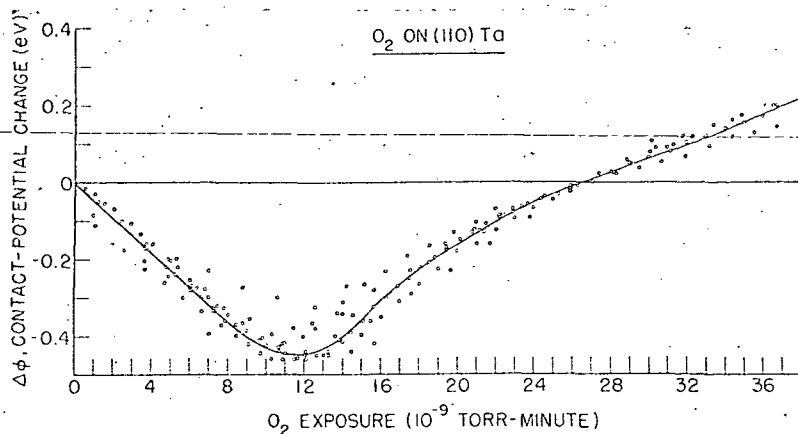


Fig. 17. Experimental results for the adsorption of O_2 on (110) Ta in the low exposure range. The actual data have been correlated by making the experimental curve for each run pass through $\Delta\phi = 0$ at $\sim 27 \times 10^{-9}$ Torr-min. All runs were made at $300^\circ K$. [From Fehrs and Stickney⁷].

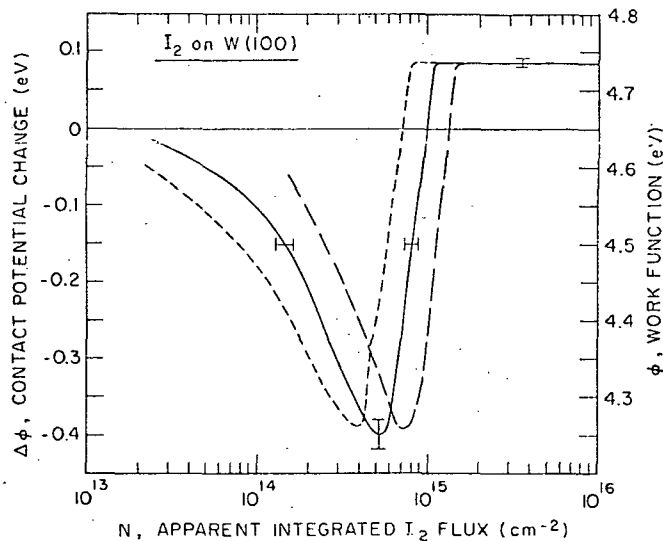


Fig. 18. Contact-potential data for the adsorption of I_2 on W(100) at $T_s = 300^\circ K$ and pressures in the range 5×10^{-9} – 1×10^{-6} Torr. The absolute work function scale on the right was derived from contact-potential results by assuming the bare surface ϕ of W(100) to be 4.65 eV. [From Fehrs and Stickney¹³.]

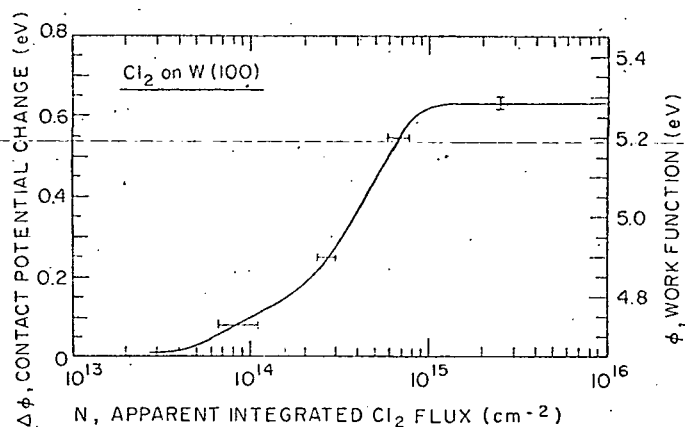


Fig. 19. Contact-potential data for the adsorption of Br_2 on $\text{W}(100)$ at $T_s \approx 200^\circ\text{K}$ and pressures in the range 5×10^{-9} – 1×10^{-5} Torr. [From Fehrs and Stickney¹³.]

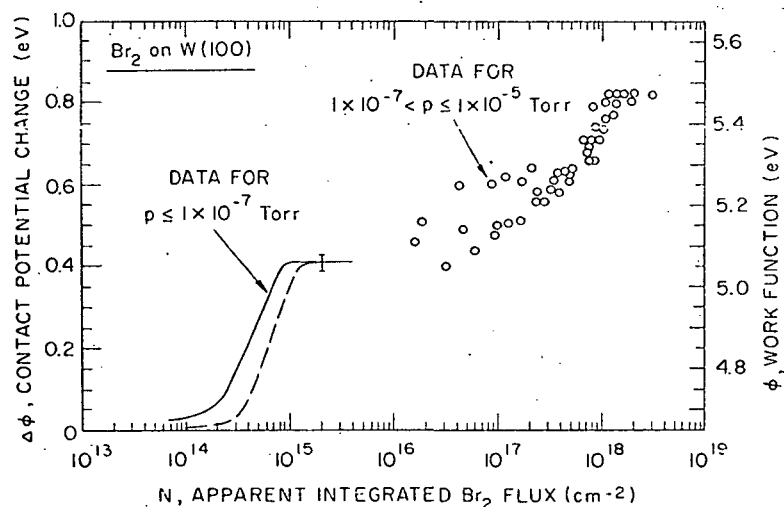


Fig. 20. Contact-potential data for the adsorption of Cl_2 on $\text{W}(100)$ at $T_s \approx 300^\circ\text{K}$ and pressures in the range 1.5×10^{-9} – 4×10^{-8} Torr. [From Fehrs and Stickney¹³.]

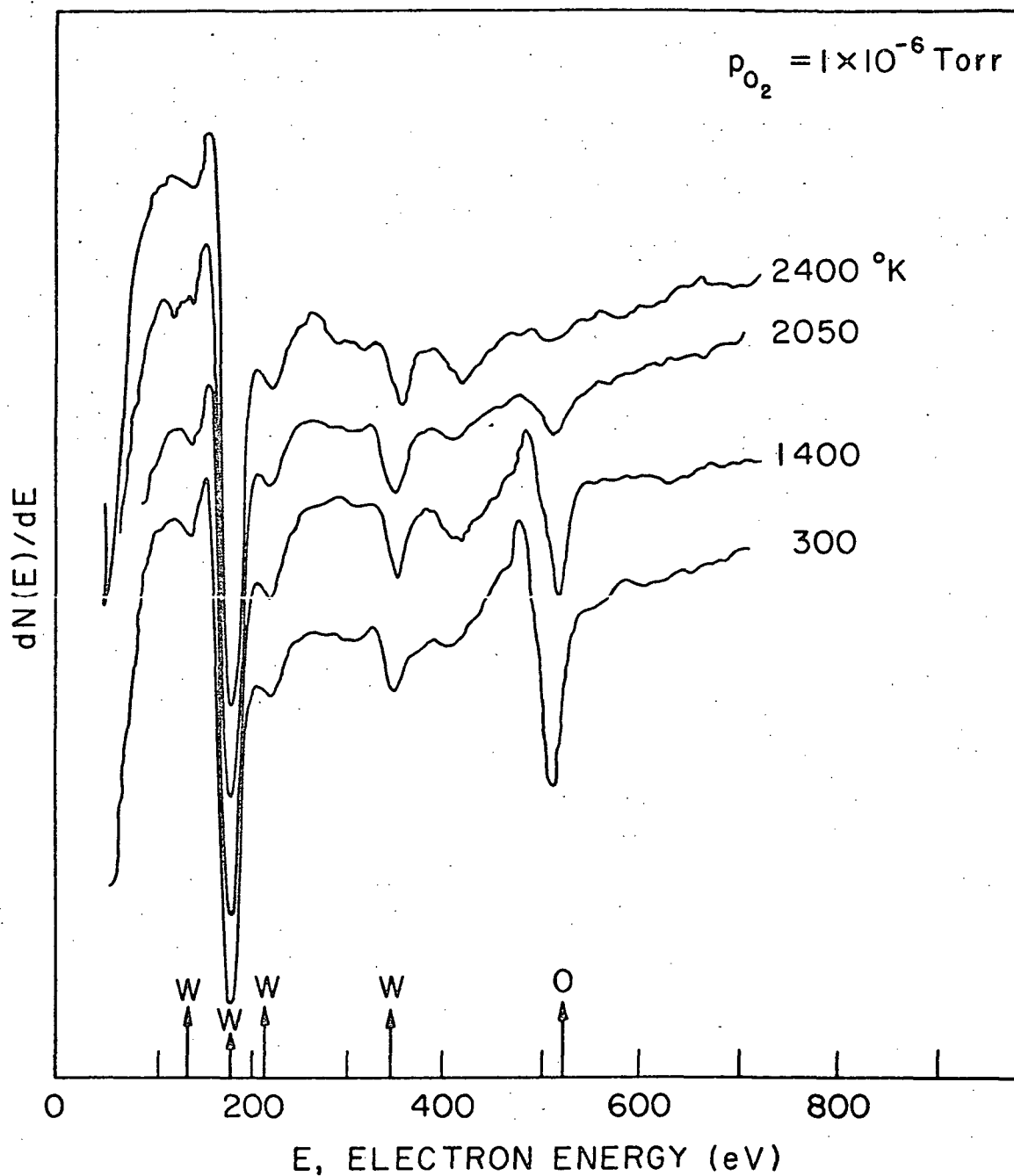


Fig. 21. Auger spectra for a polycrystalline tungsten surface exposed to O_2 at $p_{O_2} = 1 \times 10^{-6}$ Torr. Notice that the amplitude of the Auger peak corresponding to oxygen decreases as the temperature of the tungsten sample is raised from 300°K to 2400°K. Also notice that the signal-to-noise ratio is very good even when the sample is at 2400°K. [From Dabiri, Aramati, and Stickney¹⁷.]

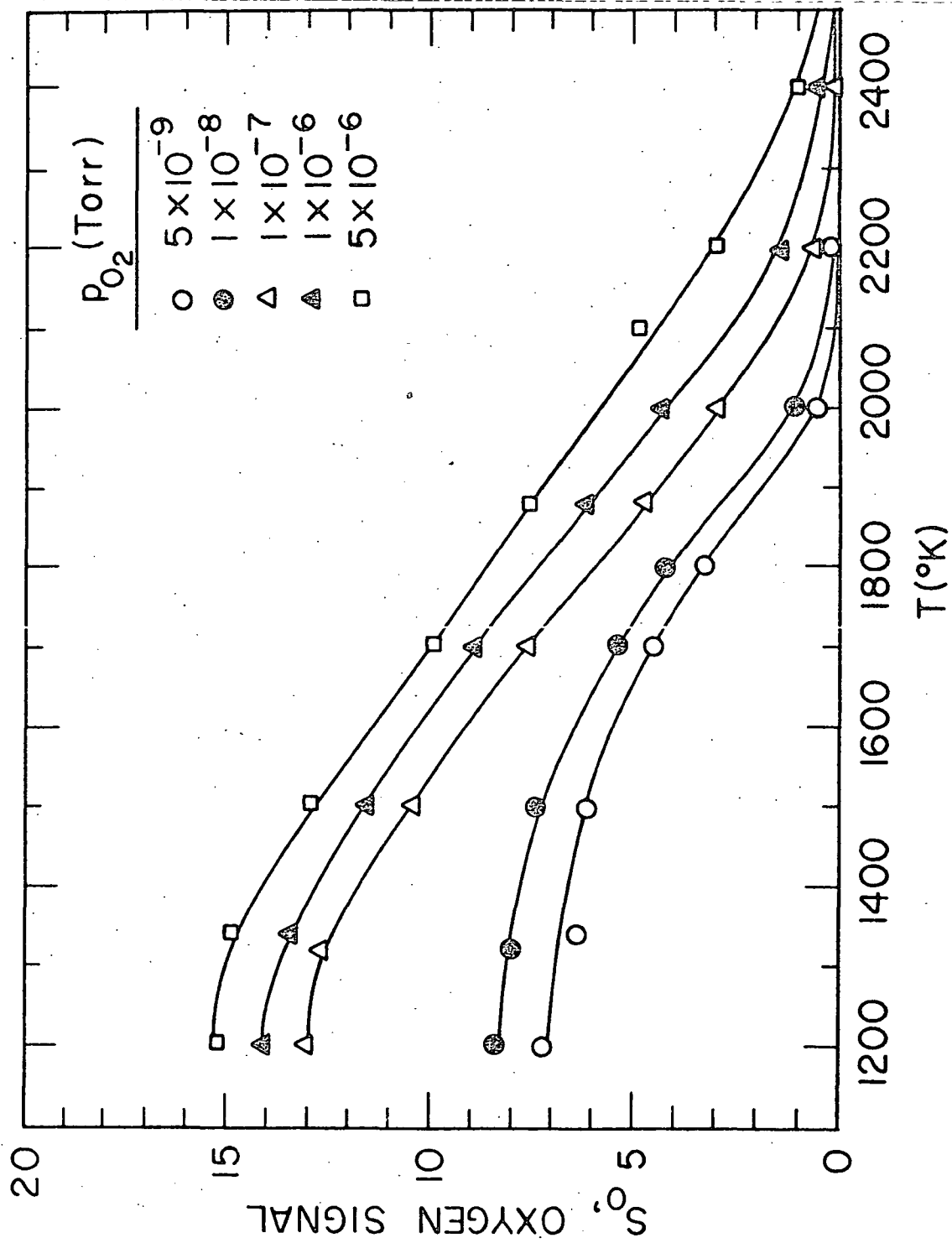


Fig. 22. Dependence of S_{O_2} , the peak to peak amplitude of the Auger peak for oxygen, on the temperature of the polycrystalline tungsten sample and on the oxygen pressure. [From Dabiri, Aramati, and Stickney¹⁷.]

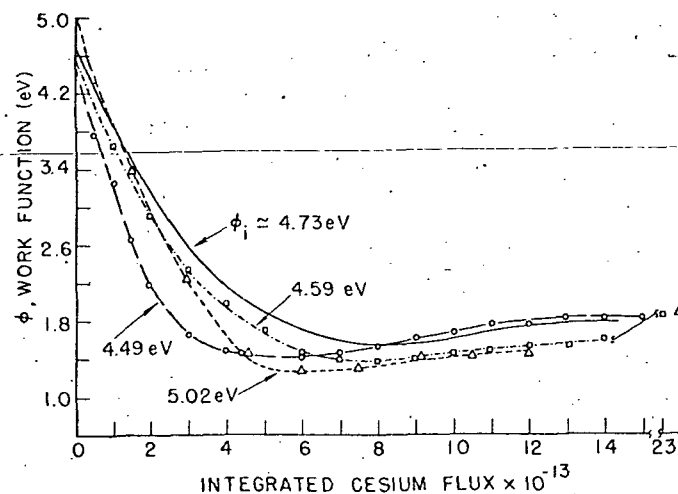


Fig. 23. Experimental results for the adsorption of Cs on oxygenated (110) Ta. Before adsorbing Cs on the surface, the initial work function, ϕ_i , was varied by adsorbing different amounts of oxygen. The experimental results for Cs adsorption on clean (110) Ta ($\phi_i = 4.73$ eV) have been included for purposes of comparison. [From Fehrs and Stickney⁷.]

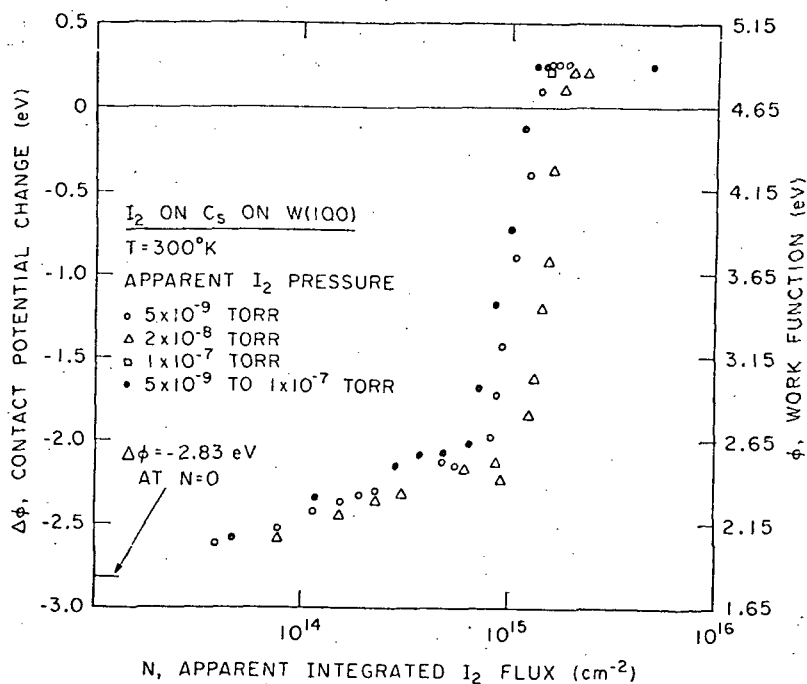


Fig. 24. Contact-potential data for co-adsorption of Cs and I_2 on W(100) at $T_s \approx 300^\circ K$. In these studies a monolayer of Cs was applied to the surface prior to I_2 adsorption. [From Fehrs and Stickney¹³.]

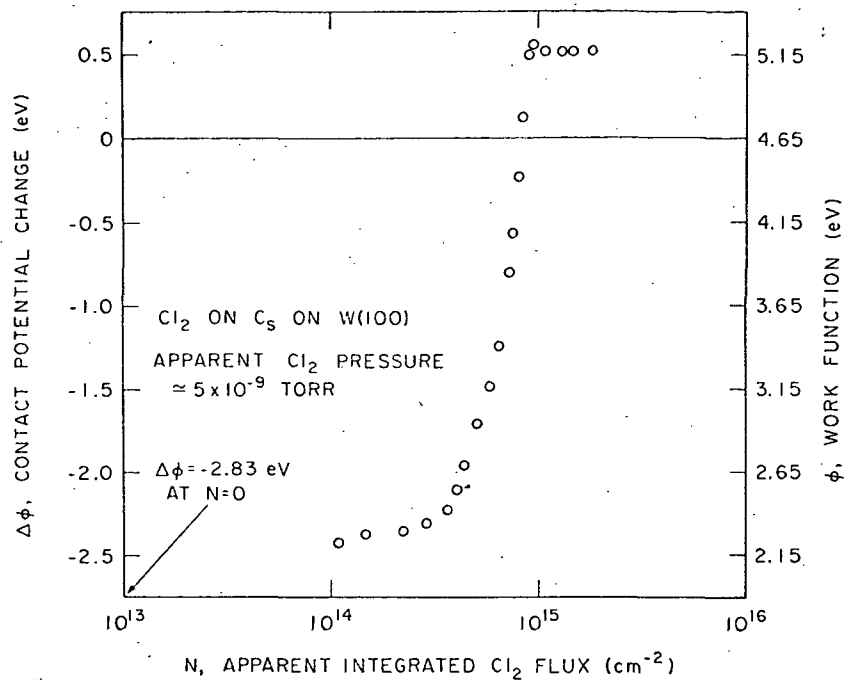


Fig. 25. Contact-potential data for co-adsorption of Cs and Cl on W(100) at $T_s \approx 300^\circ\text{K}$. In this study a monolayer of Cs was applied to the surface prior to Cl_2 adsorption. [From Fehrs and Stickney13.]

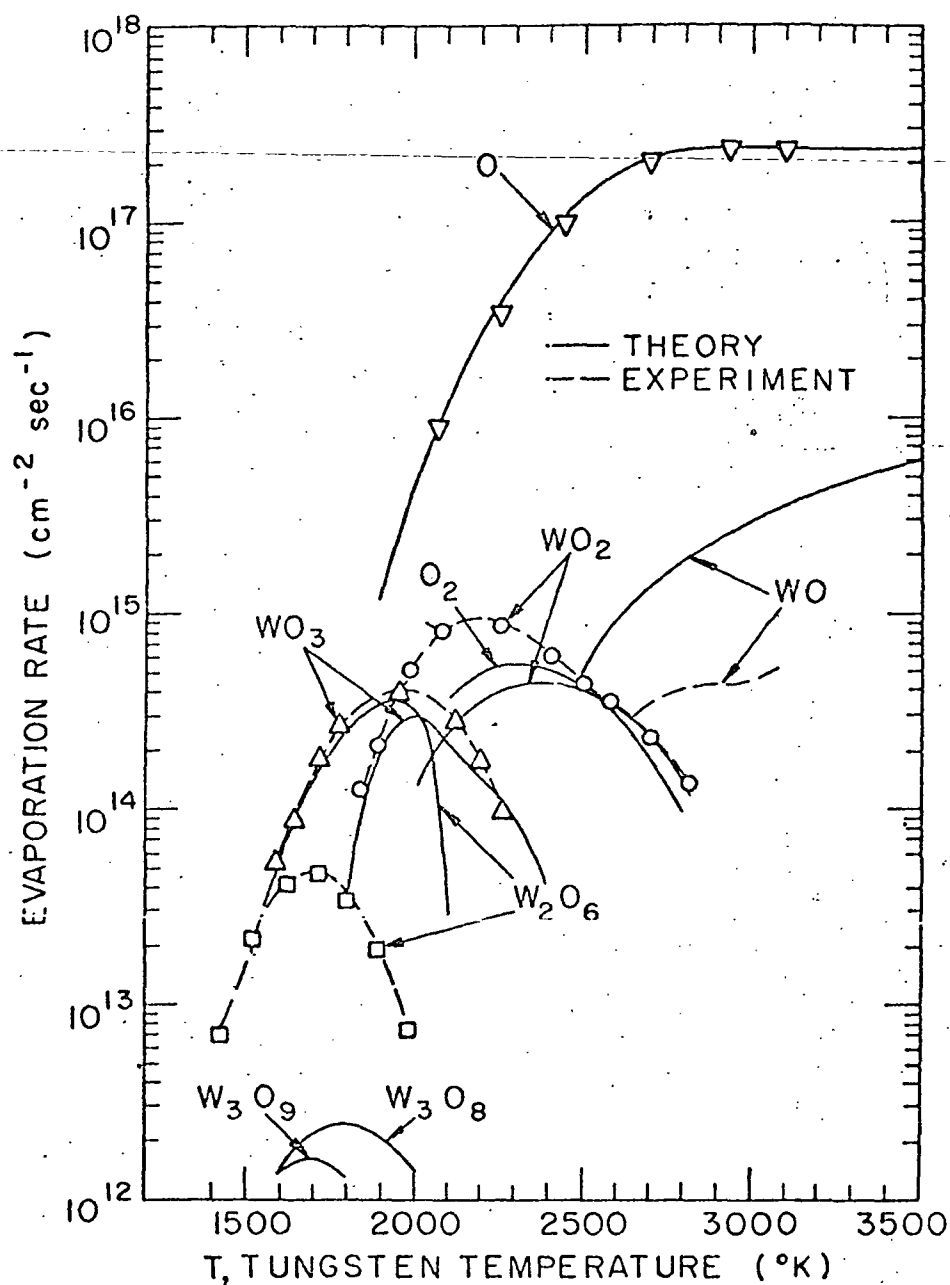
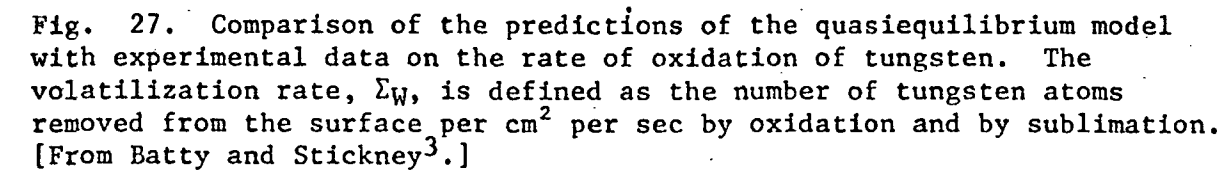


Fig. 26. Comparison of the predictions of the quasiequilibrium model with the mass spectrometric data of Schissel and Trulson on the evaporation rates of volatile species formed in the chemical reaction of gaseous O_2 with solid tungsten. The experimental data were obtained at constant O_2 pressure (2.1×10^{-4} Torr) and constant O_2 temperature ($\sim 300^\circ K$), corresponding to an impingement rate of $Z_{O_2}^i = 7.5 \times 10^{16} \text{ cm}^{-2} \text{ sec}^{-1}$. [From Batty and Stickney¹.]



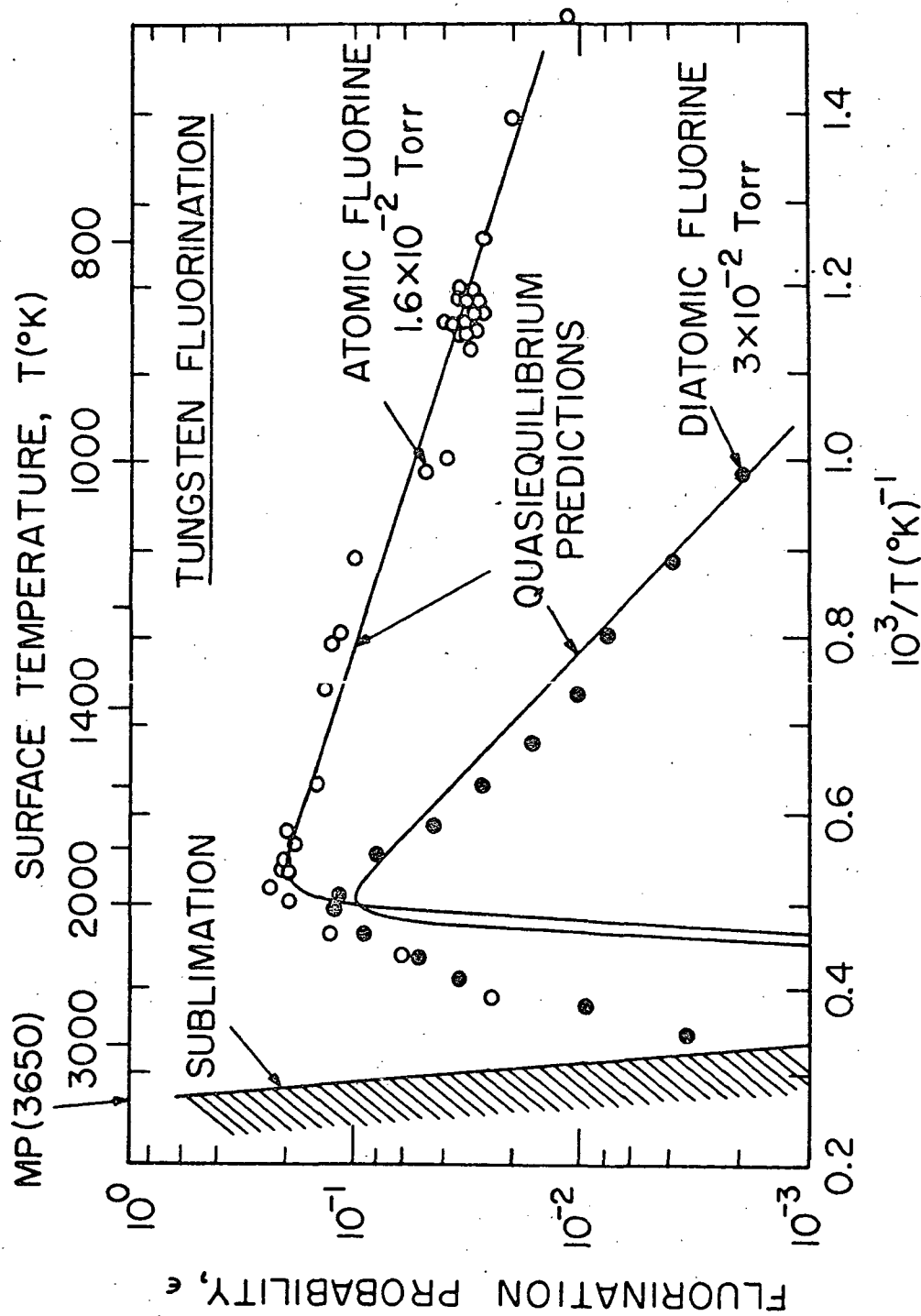


Fig. 28. Comparison of predictions of the quasiequilibrium model with experimental data of Rosner and Allendorf, where the fluorination probability ϵ , is defined as the ratio of the rate of removal of W atoms from the specimen to the rate at which fluorine atoms or molecule impinge upon the specimen. [From Abbott and Stickney¹⁹.]